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2017 J. Phys.: Conf. Ser. 789 012057

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# Application of low pressure capacitively coupled rf hydrogen plasma for low temperature reduction of iron clusters in structure of fe-pillared materials

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**Abstract.** The unique properties of pillared materials determine their use in catalysis, purification and separation. The paper studies the reduction of composite catalysts, Fe-pillared materials. The authors compare their reduction in low temperature capacitively coupled RF hydrogen discharge of low pressure to their conventional direct hydrogen reduction in a tubular muffle furnace. X-ray diffraction analysis was used to characterize the iron-bearing phases. The results show that the reduction of iron hydro/oxide clusters associated with an aluminosilicate matrix to metallic iron is very challenging due to the degree of the pore space availability for hydrogen.

## 1. Introduction

Chemical behavior in extreme and unconventional conditions has been widely studied in applied research papers. Innovative approaches, however, promise to increase the reaction rate, product yield, selectivity and to reach milder reaction conditions in chemical synthesis. In recent decades, the use of plasma chemical reactions has been a subject of considerable attention and research in this field.

The chemistry of hydrogen reduction of metals from oxides is well known. In accordance with the principle of Baikov's transformation sequence [1] the process of iron reduction from oxides proceeds stepwise by successive transition from higher oxides to lower ones. Also, according to Baikov, hydrogen is the best option of the three gases ( $H_2$ ,  $CO_2$ ,  $CH_4$ ), which can be used for reduction processes.

In experimental practice, hydrogen reduction of metal oxides is usually carried out using high-temperature plasma. Non-equilibrium plasma possesses an advantage of high energy, which is sufficient to generate atomic hydrogen, excited hydrogen molecules and other active particles, stimulating reduction process at low gas temperatures and solid oxides. The main problem of non-thermal plasma metallurgy is associated with the secondary surface reaction kinetics and gas-phase products (particularly water vapor) desorption efficiency to provide a sufficient number of active plasma particles penetrating into the deeper layers of solid oxides. Another problem is the discharge power and, therefore, productivity of non-thermal plasma metallurgy.



Atomic hydrogen generated in non-thermal plasma reaches the solid metal oxide surface by stimulating the 'cold' reduction process. The process can be influenced by vibration-excited  $H_2$  molecules by such factors as its surface decomposition and  $H$  atom diffusion in a crystalline structure.

The surface temperature in non-equilibrium discharges can be higher than the gas temperature, which is the effect of non-equilibrium surface heating. This effect can stimulate the surface oxide reduction process while keeping low gas temperature, therefore, the  $H_2$  decomposition efficiency in the plasma is high [2]. In the presence of hydrogen atoms and ions, generated in the plasma discharge, the reduction of metals from oxide can be observed at room temperature [3].

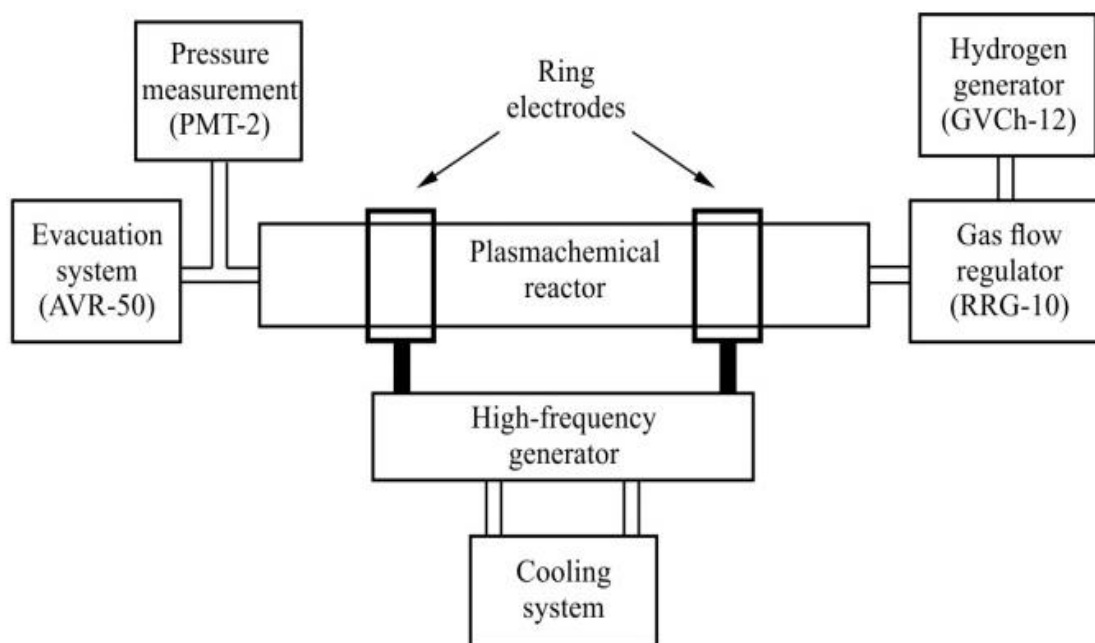
The use of easily available and inexpensive natural layered minerals with a high specific surface area and catalytic activity for petrochemical industry processes is promising. The fundamental limitation for the use of natural layered minerals as catalysts and carriers is its low thermal stability (dehydration leads to the interlayer space collapse).

This problem can be solved by modifying the natural layered minerals using different chemical and physical methods. The intercalation of large size polyvalent metals, oligo-/polycations (with a structure similar to Keggin cation), in the interlayer space of layered silicates allows for obtaining composite materials (pillared materials) with a defined porosity, high specific surface and a defined catalytic activity depending on the selected cation.

Theoretically, plasma chemical technologies can ensure reduction of the iron compounds (of oxide or hydroxide forms) in the interlayer space to +2 or 0 rate of oxidation. If proven experimentally, the use of these technologies may be promising for the production of pillared structures based on layered silicates and iron compounds in different oxidation rates.

## 2. Methods

The object under investigation is a sample of dispersed powder pillared material (Fe-PM) obtained using a definite method [4].



**Figure 1.** Circuit diagram of plasma chemical hydrogen setup.

Classical direct hydrogen reduction was carried out in a tubular muffle furnace. 0.2 g of the sample was placed in a silica boat and kept at 450°C for 3 hours in a hydrogen stream at atmospheric pressure.

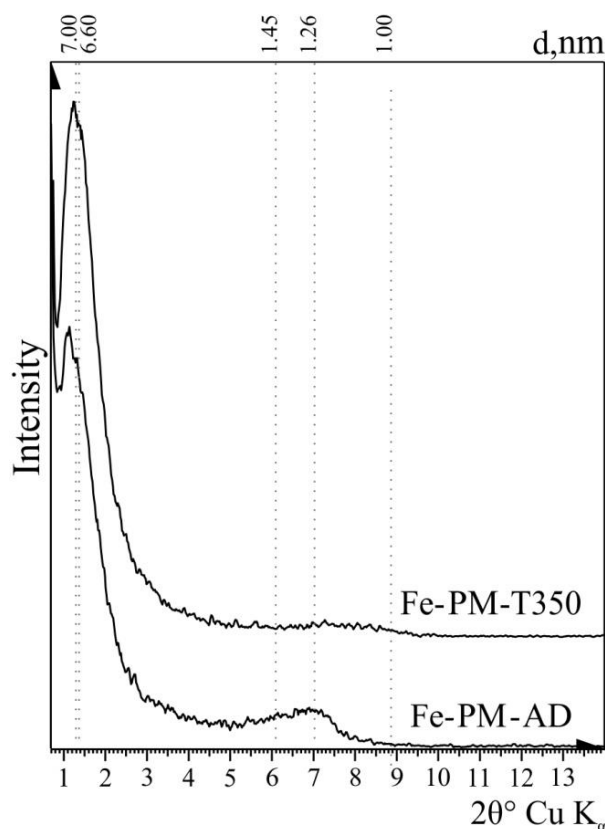
Plasma chemical reduction of the Fe-PM powder was performed in a cylindrical hydrogen plasma chemical quartz glass reactor under conditions chosen by the authors previously [5]. The circuit diagram is shown in Figure 1.

The diffraction spectra of powder and oriented samples were recorded on the D2 Phaser diffractometer produced by Bruker Axs GmbH with the standard Bragg-Brentano ( $\theta$ - $\theta$ ) geometry on reflection and the 141.4 mm goniometer radius.  $\text{CuK}\alpha$  radiation (30 kV, 10 mA), fixed slits, and a linear position-sensitive LYNXEYE detector and sample rotation in its own plane were used. The obtained diffraction spectra were processed in DIFFRAC.SUITE package software. The phases were identified in the diffraction data ICDD PDF-2 Release 2013 with the DIFFRAC.EVA module software. Quantitative calculation of the individual phases was carried out by Rietveld method using the DIFFRAC.TOPAS module software.

Samples: Fe-PM-AD – air dried at room temperature sample, Fe-PM-T350 – heat-treated at 350 °C, Fe-PM-450H2 conventional hydrogen reduction at 450 °C, Fe-PM-P – plasma chemical reduction.

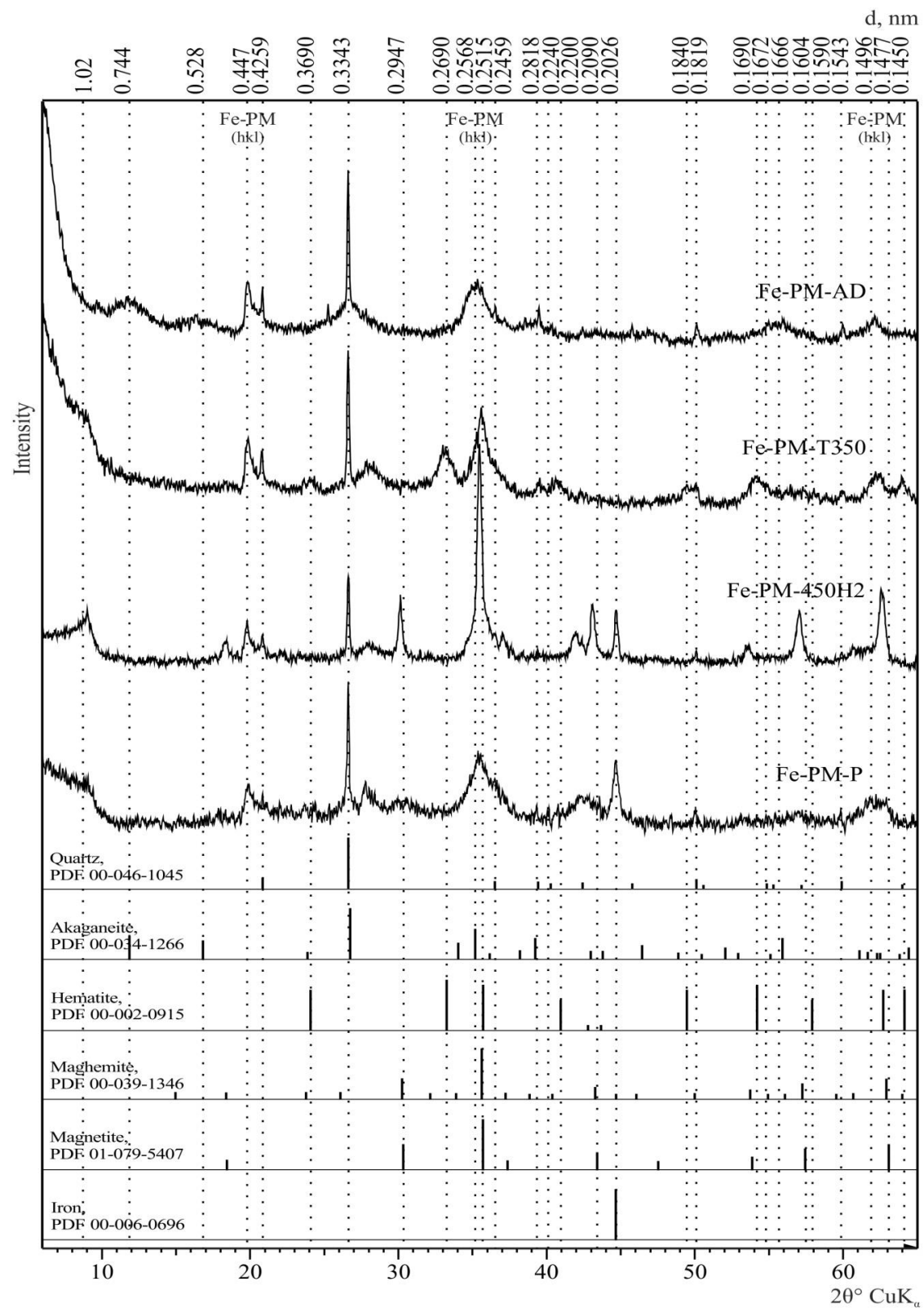
### 3. Results and Discussion

Figure 2 shows the diffraction patterns of air-dried and heat-treated oriented Fe-PM samples. After thermal treatment at 350°C, the structure keeps stability, showing the interlayer distance value of 6.6 nm.



**Figure 2.** X-ray diffraction patterns of oriented Fe-pillared materials samples before and after thermal treatment.

The increase of the distance between silicate layers compared to  $\text{Na}^+$ -form ( $d=1.25$  nm) and the stability of the structure during thermal treatment have to ensure the availability of porous space and iron oxide phase clusters associated with the silicate matrix for the penetration of hydrogen molecules and iron reduction.



**Figure 3.** X-ray diffraction patterns of powder Fe-pillared materials samples under different exposure.

Figure 3 shows the diffraction patterns of the powder Fe-PM samples under different exposures. The iron in air dried sample is in akaganeite phase. Fe-PM thermal treatment in the air leads to the formation of hematite and maghemite phases. Conventional reduction by hydrogen during 3 hours leads to the formation of the magnetite, wustite and metallic iron phases.

Plasma chemical hydrogen reduction also leads to a more reduced oxide phases and metallic iron, but the diffraction peaks shape has a lower intensity and a larger FWHM. Table 1 shows the percentage ratio of iron-containing phases (calculated for 100% without the silicate phases) and their average coherent scattering region sizes (CSR).

**Table 1.** The ratio of iron-containing phases and their average CSR size for Fe-PM samples.

Sample	Phase content, % CSR, nm					
	Akaganeite ( $\beta$ -FeOOH)	Hematite ( $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> )	Maghemite ( $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> )	Magnetite (Fe <sub>3</sub> O <sub>4</sub> )	Wustite (FeO)	Iron ( $\alpha$ -Fe)
Fe-PM-AD	$\frac{100}{5.0 \pm 0.2}$	-	-	-	-	-
Fe-PM-T350	-	$\frac{63}{12.0 \pm 0.6}$	$\frac{37}{7.0 \pm 0.7}$	-	-	-
Fe-PM-450H2	-	-	-	$\frac{73}{32.7 \pm 0.7}$	$\frac{21}{12.7 \pm 0.4}$	$\frac{6}{57.0 \pm 5.6}$
Fe-PM-P	-	-	-	$\frac{67}{5.7 \pm 0.4}$	$\frac{21}{9.0 \pm 1.2}$	$\frac{12}{26.6 \pm 2.3}$

The table shows that in case of conventional reduction in a hydrogen stream at atmospheric pressure and 450°C, the crystallite size of the iron metal phase is more than two times higher for metallic iron and six times higher for magnetite than that after low pressure capacitively coupled RF hydrogen plasma treatment. Therefore, plasma chemical reduction occurs in milder conditions.

#### 4. Conclusion

According to the experimental results, the use of plasma chemistry for the reduction of clusters of iron-containing compounds in the composite catalysts is reasonable, because this treatment does not lead to intense crystallization of metal phase due to milder reaction conditions (low temperature).

In spite of the higher temperature and hydrogen concentration in conventional recovery, it gives the same amount of iron as the plasma chemical method. In consideration of the substantial differences between the methods, it is obvious, that the reduction process of iron in the structure of the Fe-PM is limited by the gas diffusion in the microporous space.

The problem of iron-containing clusters availability for hydrogen cannot be solved only by the synthesis of Fe-pillared materials with sufficiently large (6.6 nm) interlayer distances, and require technological solutions to increase the diffusion rate and provide minimal high reduction temperature.

#### Acknowledgments

The work has been performed under the support of the Ministry of education and science of the Russia Federation, project No. 2196 of 01.02.2014.

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